

Magnetic stress as a driving force of structural distortions: the case of CrN

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We show that the observed transition from rocksalt to orthorhombic P_{nma} symmetry in CrN can be understood in terms of stress anisotropy. Using local spin density functional theory, we find that the imbalance between stress stored in spin-paired and spin-unpaired Cr nearest neighbors causes the rocksalt structure to be unstable against distortions and justifies the observed antiferromagnetic ordering. This stress has a purely magnetic origin, and may be important in any system where the coupling between spin ordering and structure is strong.

71.15.Mb, 75.25.+z, 75.40.Mg, 75.80.+q

The simultaneous occurrence of structural distortion and change of magnetic ordering is observed in several magnetic compounds. In general, the interplay between structural and spin degrees of freedom depends on the detailed configuration of the electronic and phonon states, and a unique picture that elucidates the coupling mechanism is missing. A large class of systems where this interplay is strong are materials containing ions with degenerate (usually e_g) orbitals (Jahn-Teller ions), such as Mn^{3+} , Cr^{2+} or Cu^{2+} [1,2]. The degeneracy causes instabilities that can be relieved by structural distortions or orbital (and eventually charge) ordering. In this paper we focus on CrN, one of the most widely employed materials in coating technology, due to the extreme hardness of CrN films. It is also the prototype material of strong magneto-structural interactions, since here, more than in any other case, the coupling is clearly revealed: at room temperature it is paramagnetic (PM) in the RS structure, like most of the transition metal nitrides, but at Néel temperature $T_N=273-286$ K, a both structural and magnetic transition to an antiferromagnetic (AFM) orthorhombic P_{nma} phase is observed [3-6].

But other compounds presents indications of strong spin and structural coupling. To name a few of them, in the perovskite $LaMnO_3$ the distortions are necessary to stabilize the observed A-type antiferromagnetic ordering. The doped cobalt perovskite $La_{1-x}Sr_xCoO_3$ exhibits unusual properties as a function of doping and temperature [7], and in the diluted magnetic semiconductors $Zn_{1-x}Cr_xSe$, the magnetic Cr^{2+} impurities are strongly affected by Jahn-Teller distortions [8]. Also large is the class of materials manifesting magnetoelastic effects, such as changes of magnetic anisotropy coupled to distortions and strains. For example, the martensitic phase transition of Ni_2MnGa from cubic Heusler to tetragonal structure is accompanied by a change in magnetic anisotropy and driven by magnetoelastic coupling. [9]. In the layered $Cu/Co/Ni/Cu/Si(001)$ the magnetic anisotropy can be induced by strain and controlled through the film thickness [10], and in $CeNiSn$ the magnetic ordering can be changed by application of uniaxial strain [11].

For all of these materials, the stress is an important

quantity, being naturally able to bridge electronic and structural properties. The stress relief argument is very popular in surface physics to explain processes like surface reconstructions, adsorptions and growth: after a structural perturbation, a stress excess is produced in the system (e.g. the surface stress), that is relieved by further structural rearrangements involving symmetry breaking and eventually change of atomic density at surface. In this paper we show that is possible to apply similar arguments to magnetic systems. Specifically, we use the concept of stress relief to explain the stability of one magnetic ordering with respect to another, and to show how the change of ordering is related to a structural distortion.

In analogy to the surface stress, we define *magnetic stress* to be the stress associated with a change of spin ordering. If O^1 and O^2 represent two magnetic phases of a system with the same structure, the magnetic stress \hat{T} associated with the transition is:

$$\hat{T} = \hat{T}^{O^1} - \hat{T}^{O^2} = \frac{\partial E^{O^1}}{\partial \hat{\epsilon}} - \frac{\partial E^{O^2}}{\partial \hat{\epsilon}}, \quad (1)$$

where $\hat{\epsilon}$ is the strain tensor. \hat{T} has a purely magnetic origin, since it originates from changes in spin orientations, not structural transitions, but may be relieved by structural transitions. We also define the magnetic stress per bond by mapping \hat{T} onto the Heisenberg model,

$$\hat{T} = - \sum_{ij} S_i \cdot S_j \hat{t}_{ij}, \quad (2)$$

where \hat{t}_{ij} is the strain derivative of the usual energy exchange interaction parameter J_{ij} , and represents the change of stress caused by turning the spin orientation on atoms i and j from parallel to antiparallel. A positive \hat{t}_{ij} means that the single spin-flip produces a tensile stress that can be relieved by shortening the i - j distance. A negative \hat{t}_{ij} , instead, represents a compressive stress that is relieved by stretching the i - j distance. The meaning of the definitions of Eqs.1 and 2 will be transparent when applied to the practical case of CrN.

Below T_N , CrN is orthorhombic, with an unusual magnetic ordering [3] (see Fig.1, left) built up by $(1\bar{1}0)$ FM

layers whose spin direction alternates up and down after each 2 layers, so that the system is antiferromagnetic (AFM) overall (in the following this phase is labeled $\text{AFM}_{[1\bar{1}0]}^2$). Along with the $\text{AFM}_{[1\bar{1}0]}^2$, we consider two other AFM phases as possible competitors: the $\text{AFM}_{[1\bar{1}0]}^1$, similar to the former but with a one-by-one compensation of FM layers along $[1\bar{1}0]$ (Fig.1, right), and the $\text{AFM}_{[111]}^1$, made by (111) FM layers alternated along $[111]$, common for some strongly ionic transition-metal oxides (e.g. MnO).

Our calculations are based on local spin density functional theory (LSD) [12], and employ plane-wave basis and Troullier-Martins pseudopotentials [13] (this methodology already described successfully some properties of CrN [14–17]). The microscopic stress tensor is calculated in LSD [18] (within the framework of the ABINIT [19] project) and problems of finite-size basis have been efficiently circumvented [20].

To rationalize the RS-to-orthorhombic transition, we can picture it as a three step process: first, an hydrostatic expansion of the volume accompanies the non spin polarized-to-spin polarized transition. This is the dominant step in terms of energy stabilization. Second, a further stabilization is obtained from the competition of different magnetic orderings with the same (cubic) structure. Third, a shear strain is applied onto the (001) plane, in accordance with the experimental finding [3]. The observed distortion consists of a reduction of the lattice parameter a and an increase of b (of $\sim 2\%$) with respect to their ideal values ($a = a_0/\sqrt{2}$, $b = b_0/\sqrt{2}$, and $c = a_0$, where a_0 is the cubic lattice constant), in a way that the Cr-N distance is unchanged. Although a second-order effect with respect to the hydrostatic expansion, we will show that the distortion is fundamental in stabilizing the observed $\text{AFM}_{[1\bar{1}0]}^2$ phase.

The effects related to the first step are described in Fig.2, where the energies and stresses of PM and FM orderings in the RS structure are shown. In the PM phase, the high density of states (DOS) at the Fermi energy (E_F) strongly drives CrN towards a Stoner instability. Although the high DOS peak at E_F disappears in the FM phase, the spin splitting does not manage to open a gap, thus, FM CrN is still a (poor) metal [17]. It is also a robust magnetic compound, with a magnetic moment ($M=2.09 \mu_B$ per Cr atom) almost entirely due to the Cr t_{2g} splitting, and a chemical configuration close to $\text{Cr}^{2+}\text{N}^{2-}$.

We find a difference of 0.182 eV/formula unit between PM and FM energies, calculated at the equilibrium a_0 of the respective phases, that are 7.72 a.u. and 7.84 a.u. for PM and FM, respectively. Thus, after polarization, the lattice constant increases $\sim 1.5\%$. This strong magnetovolume effect is related to a large magnetic stress. At the PM lattice constant (where T^{PM} is zero by definition), the spin-polarization produces a compressive stress

$T^{FM}=1.89$ eV/formula unit, whose relief corresponds to an energy gain $\Delta E^{FM}=T^{FM} \Delta a/a \simeq 0.03$ eV/formula unit.

The increase in compressive stress is a consequence of some charge localization (mostly Cr $d t_{2g}$ charge) around the Cr nucleus, due to the spin polarization. The charge localization increases the kinetic stress, and, in turn, decreases the tensile electron-ion interaction.

Within this expanded volume, but still retaining the RS symmetry, we consider the competition among different magnetic orderings (the calculated lattice constant is quite similar for FM and AFM, i.e. a change of magnetic ordering does not produce that significant hydrostatic compression). We find (Table I) all the AFM phases are favored over the FM one. Moreover, the $\text{AFM}_{[1\bar{1}0]}^1$, and not the observed $\text{AFM}_{[1\bar{1}0]}^2$, is the stable phase in the RS structure.

The density of states (DOS) of a single Cr ion in the $\text{AFM}_{[1\bar{1}0]}^2$ phase is shown in Fig. 3. The Cr configuration is nearly Cr^{2+} , with magnetization $M=2.12 \mu_B$. Notice that in the (001) plane of the orthorhombic cell, the t_{2g} orbitals (whose DOS is drawn by the shaded area in the Figure), not the e_g s, are directed along \hat{x} and \hat{y} . The e_g orbitals are non degenerate, due to the AFM symmetry, and each of them is occupied by nearly half an electron. Their total contribution to the magnetization is only $\sim 0.2 \mu_B$. The exchange splitting for t_{2g} orbitals is ~ 2 eV, with the t_{2g}^\uparrow almost completely filled. The global t_{2g} occupation is 2.76, and the contribution to the magnetic moment is $1.9 \mu_B$.

We can understand the competition among spin orderings by a two-parameter Heisenberg model, taking into account the nearest neighbor Cr-Cr (J_1), and the next nearest neighbor Cr-N-Cr interactions (J_2). The calculated parameters are $J_1=-9.5$ meV, and $J_2=4$ meV. For the Cr-N-Cr interaction there is competition between superexchange (AFM) and double-exchange (FM) mechanisms involving Cr e_g and N p orbitals ($dp\sigma$ hybridization). The resulting coupling is slightly FM (i.e. J_2 is positive). The direct Cr-Cr coupling, instead, is mediated by t_{2g} orbital interactions ($dd\sigma$), and is AFM (i.e. J_1 is negative), as we may argue assuming, as usual, the Hund's rule. The formal equivalence of Cr^{2+} and Mn^{3+} ions may suggest some similarities between CrN and LaMnO_3 . Indeed, in both of them the magnetic ion is surrounded by an octahedral cage of cations. However, in LaMnO_3 the Mn coupling via oxygens is the only relevant interaction, whereas, for CrN the Cr-N-Cr coupling is smaller than the direct Cr-Cr AFM coupling. As a consequence, the stability increases with the number of AFM nearest neighbors (8 for the $\text{AFM}_{[1\bar{1}0]}^1$, 6 for $\text{AFM}_{[1\bar{1}0]}^2$ and $\text{AFM}_{[111]}^1$). Also, due to the symmetry of the Cr fcc sublattice, no other arrangement with more than 8 AFM nearest neighbors is possible. In other words, the signs

of J_1 and J_2 rule out the possibility that other orderings, not taken into account here, might be more stable.

On top of the RS structure, we finally apply a shear strain ϵ onto the (001) plane of the competing phases $\text{AFM}_{[1\bar{1}0]}^1$ and $\text{AFM}_{[1\bar{1}0]}^2$ (Table II). First consider the stress values for the undistorted (i.e. $\epsilon = 0$) structure: the $\text{AFM}_{[1\bar{1}0]}^2$ phase is under a condition of appreciable stress with respect to the $\text{AFM}_{[1\bar{1}0]}^1$. This stress originates from the spin ordering asymmetry on the (001) plane: in the $\text{AFM}_{[1\bar{1}0]}^2$ phase, each Cr has two spin-antiparallel nearest neighbors along \hat{x} , and two spin-parallel along \hat{y} . The bonds between AFM neighbors are under condition of tensile stress (i.e. $T_{xx} > 0$), whereas the bonds between FM neighbors store compressive stress (i.e. $T_{yy} < 0$). Clearly, a planar distortion will be able to relieve the stress and lower the energy of the $\text{AFM}_{[1\bar{1}0]}^2$. In contrast, the $\text{AFM}_{[1\bar{1}0]}^1$, which is isotropic on (001), cannot undergo the same stabilization: each Cr has two spin-parallel nearest neighbors in both \hat{x} and \hat{y} directions, and the eventual energy gain due to the stretch along \hat{y} would be lost due to the compression along \hat{x} . Also, T_{zz} is different for the two phases: in the $\text{AFM}_{[1\bar{1}0]}^2$, the larger number of FM Cr-Cr bonds having an orthogonal component causes an excess of compressive stress along \hat{z} .

Applying Eq.2 we can express the stress (at $\epsilon=0$) in terms of exchange-interaction parameters. For a planar strain on (001), we have three independent parameters corresponding to the in-plane Cr-Cr bonds (t_1), and the planar and orthogonal components of the out-of-plane Cr-Cr bonds (t_{2x} and t_{2z}). Our results gives $t_1=1.04$ eV, $t_{2x}=0.24$ eV, and $t_{2z}=0.20$ eV. Thus, the parallel-to-antiparallel spin flip causes a significantly large tensile stress for the Cr-Cr bonds parallel to (001).

On the basis of the magnetic stress results at $\epsilon=0$ we are able not only to predict the occurrence of the distortion for $\text{AFM}_{[1\bar{1}0]}^2$, but also to estimate the energy gain due to the stress relief. Indeed, a 2% distortion gives an energy gain $\Delta E = (T_{xx} - T_{yy}) \frac{\delta a}{a} \sim 0.04$ eV which is enough for the $\text{AFM}_{[1\bar{1}0]}^2$ to be stabilized over the $\text{AFM}_{[1\bar{1}0]}^1$. This estimation can be compared with the direct calculation of energies and stresses at $\epsilon \neq 0$. As expected, the distortion progressively relieves the stress and stabilizes the observed phase. Our results gives a theoretical distortion slightly larger than the experimental value: at $\epsilon = 4\%$ most of the planar stress is relieved. In contrast, the distortion on the $\text{AFM}_{[1\bar{1}0]}^1$ increases the stress and is energetically unfavorable.

The stabilization of $\text{AFM}_{[1\bar{1}0]}^2$ ordering is ultimately due to different stress stored in the bonds between spin-antiparallel and spin-parallel Cr nearest neighbors. Stress asymmetry and ordering of t_{2g} orbitals are intimately related: since the Cr-Cr interaction occurs via direct t_{2g} coupling and is AFM, J_1 should vanish in the

limit of large nearest neighbor distance, whereas a shortening of the distance should increase the overlap between t_{2g} orbitals, making J_1 even more negative.

This explains why a bond contraction stabilizes the spin-antiparallel interactions, while a bond stretching stabilizes the spin-parallel interactions. In Fig.4 we show the DOS of d_{x^2} and d_{y^2} orbitals (that contribute most to the Cr-Cr planar coupling) for the undistorted $\text{AFM}_{[1\bar{1}0]}^2$ ordering (obviously they are degenerate for $\text{AFM}_{[1\bar{1}0]}^1$). The tendency of these orbitals to increase the overlap (and, thus, the hybridization) along \hat{x} , and to stay more localized along \hat{y} is clearly visible.

In conclusion, in this paper we have given a definition of magnetic stress, and proposed it as a tool for understanding and predicting the subtle relations between magnetic ordering and structural properties. For CrN, we show that the coupling between the $\text{AFM}_{[1\bar{1}0]}^2$ ordering and the orthorhombic P_{nma} structure is driven by the relief of tensile stress stored in the AFM Cr nearest neighbors, and associated with the direct interaction of t_{2g} orbitals. Our results for CrN may stimulate the application of arguments based on stress relief to many other magnetic compounds. Indeed, the predictive power of the stress should be important in every case where magnetism and structural properties are strongly related.

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	AFM ¹ _[110]	AFM ² _[110]	AFM _[111]	FM
E	0	0.034	0.050	0.075

TABLE I. Energies E (in eV/formula unit) of RS CrN for different magnetic orderings, calculated at the respective theoretical lattice constants. All the values are relative to that of the AFM¹_[110], that is the most stable phase overall, as long as the distortion from cubic symmetry is not considered.

	AFM ¹ _[110]			AFM ² _[110]		
ϵ	0%	2%	4%	0%	2%	4%
E	0	0.007	0.040	0.034	-0.020	-0.028
T_{xx}	0	-0.45	-0.81	1.13	0.79	0.19
T_{yy}	0	0.41	1.03	-0.95	-0.55	-0.27
T_{zz}	0	-0.02	0.00	-0.78	-0.76	-0.68

TABLE II. Energies E (in eV/formula unit) and stresses \hat{T} (eV/formula unit) for AFM¹_[110] and AFM²_[110] CrN as a function of the applied (001) planar strain ϵ . The corresponding changes of lattice parameters are $\delta a = -\epsilon a$, and $\delta b = \epsilon b$, i.e. the \hat{x} axis is compressed, and the \hat{y} is stretched. All values are relative to that of the undistorted AFM¹_[110] phase.

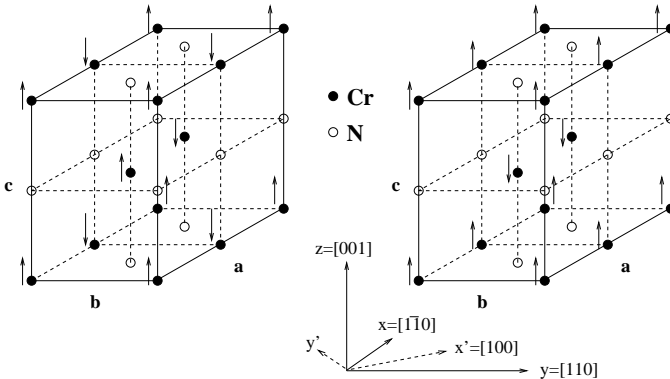


FIG. 1. Orthonormal cell of CrN (4 formula unit) in the observed AFM²_[110] spin ordering (left) and in the AFM¹_[110] ordering (right). The cartesian axes of the cubic cell (x' and y') are rotated 45° with respect to x and y .

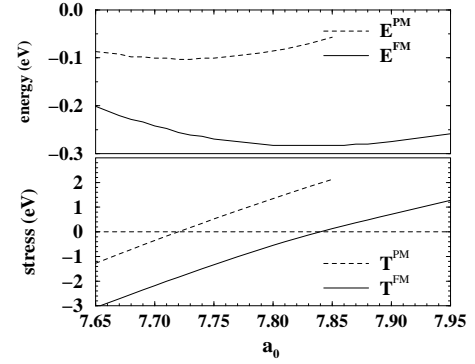


FIG. 2. Energies and stresses (per formula unit) of PM and FM phases of RS CrN, as a function of the lattice constant a_0 .

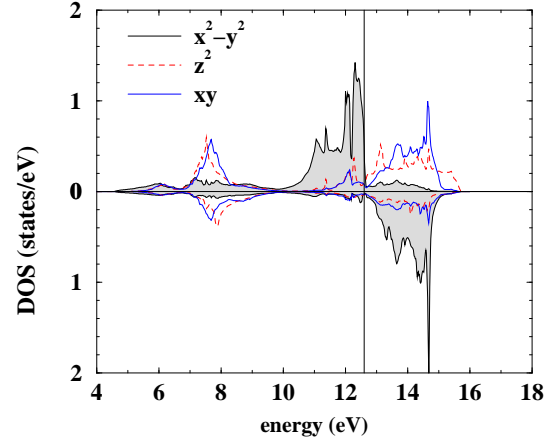


FIG. 3. Orbital-resolved DOS of one Cr ion in the AFM²_[110] CrN (undistorted). Due to the 45° rotation of the (001) plane, $d_{xy}=d_{x'^2-y'^2}$ and $d_{x'y'}=d_{x^2-y^2}$, where x' and y' are the axes of the cubic cell (see Fig. 1). The vertical line corresponds to the Fermi energy.

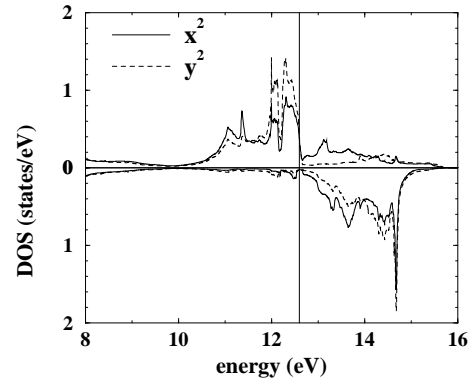


FIG. 4. DOS of Cr d_{x^2} and d_{y^2} orbitals in the AFM²_[110] RS phase. The vertical solid line corresponds to the Fermi energy.